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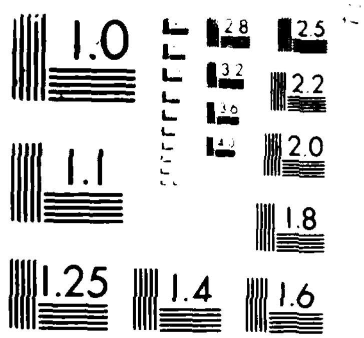
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An Automated Vapor-Generation Instrument for the Testing of Chemical Microsensors

JAY W. GRATE

Surface Chemistry Branch
Chemistry Division

DAVID S. BALLANTINE, JR.

Geo-Centers, Inc.
4710 Auth Place
Suitland, MD 20746

HANK WOHLTJEN

Microsensor Systems, Inc.
P.O. Box 90
Fairfax, VA 22030

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An instrument has been built which can generate up to twelve different vapors from bubbler or permeation tube sources. These vapors can be randomly selected, diluted to concentrations typically in the range of 1 to 10,000 mg/m^3 volume, and delivered at a programmable flow rate to the system output. Mixtures of two vapors can also be easily generated. The system is fully automated using a small personal computer and permits completely unattended operation during elaborate vapor exposure sequences. Parameters describing the vapor test conditions are automatically stored in the computer disk memory along with the sensor responses to the test. This instrument has proved to be extremely valuable for rapidly testing prototype chemical sensors.

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CONTENTS

AN AUTOMATED VAPOR-GENERATION INSTRUMENT FOR THE TESTING OF CHEMICAL MICROSENSORS

INTRODUCTION

The development of any chemical vapor sensor device is not complete until it has been repeatedly exposed to a variety of challenge vapors. These vapors should include those for which the sensor was designed to be sensitive, as well as others that may appear as significant interferences in the environment monitored by the sensor. Furthermore, truly realistic evaluation of the sensor performance requires that the device response be measured while exposed to mixtures of the target vapor and interference vapors. The generation of arbitrary vapors at arbitrary (but well known) concentrations in arbitrary sequences and mixtures is not a trivial problem.

The system reported here is designed to meet the requirements of a complete chemical vapor sensor research and development program. It is unique in its ability to generate a number of vapors (i.e. 12) from either neat chemical liquid bubblers or calibrated permeation tubes. These vapor streams can then be diluted, using computer controlled electronic mass flow regulators, to cover a wide range of conentrations. The system is also unique in its ability to maintain a contant flow rate of vapor supplied to the sensor device being tested, regardless of th carrier gas flow rate required to perform the desired vapor

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dilution. This is accomplished using a novel servo controlled piezoelectric shunt valve which diverts all vapor flow in excess of the amount programmed to be supplied to the sensor device. Finally, the system is unusual in its ability to generate mixtures of low concentration target vapors derived from a permeation tube and high concentraton interference vapors derived from bubblers. Such capability is essential for studying sensor performance under realistic conditions. The fully automated character of this instrument affords many advantages including unattended operation during long sequences of tests, reduced operator exposure to toxic chemicals and improved measurement precision.

Numerous techniques have been developed for generating precise concentrations of individual vapors [1]. In general, dynamic methods that involve the addition of calibrated amounts of vapor to a flowing stream of carrier gas are preferred. These methods minimize the effects of wall adsorption on calibration accuracy and a wide range of concentrations can be prepared by simple manipulation of the gas flow rates. This system uses dynamic vapor generation methods exclusively. Vapors can be supplied to the carrier gas by the use of thermostatted permeation tubes [2] or bubblers as vapor sources. The permeation tube mass flow rate is determined by the selection of permeation barrier area and thickness, and is calibrated by periodic weighing. The mass flow rate of the bubbler depends on the vapor pressure of the liquid, the degree to which the carrier gas becomes saturated with the vapor, and the flow rate of the carrier gas. The use of electronic mass flow controllers in this

instrument assures that the carrier gas flow rate will be constant regardless of changes in downstream flow conditions. The degree of saturation depends on the efficiency of the bubbler and the amount of liquid it contains. These variables can be controlled and reliable mass flow rates are determined gravimetrically. Unlike the permeation tubes whose weight loss is measured over a period of time, the bubblers are calibrated by passing their effluent into a charcoal filter to totally trap the vapor. The mass increase of the trap over time gives the mass flow rate.

After a "concentrated" vapor stream has been generated it can be diluted downstream with additional carrier gas. The concentration can be diluted to less than five percent of its initial value by this instrument. This results in vapor streams from permeation tubes which are typically in the range of 1 to 100 mg/m^3 and bubbler streams in the range of 100 to 100,000 mg/m^3. To generate mixtures, the flow form a permeation tube and a bubbler can be combined prior to further dilution. A regulated flow rate of the final vapor stream is available at the output of the instrument which is sent to the sensor(s). This output can be switched (under computer control) between the clean carrier gas and the vapor stream so that the zero drift and reversibility of the sensor can be readily observed. Sensor data can be collected and stored using the same computer that controls the instrument, or by a second computer in communication with the first. A system diagram is shown in Figure 1.

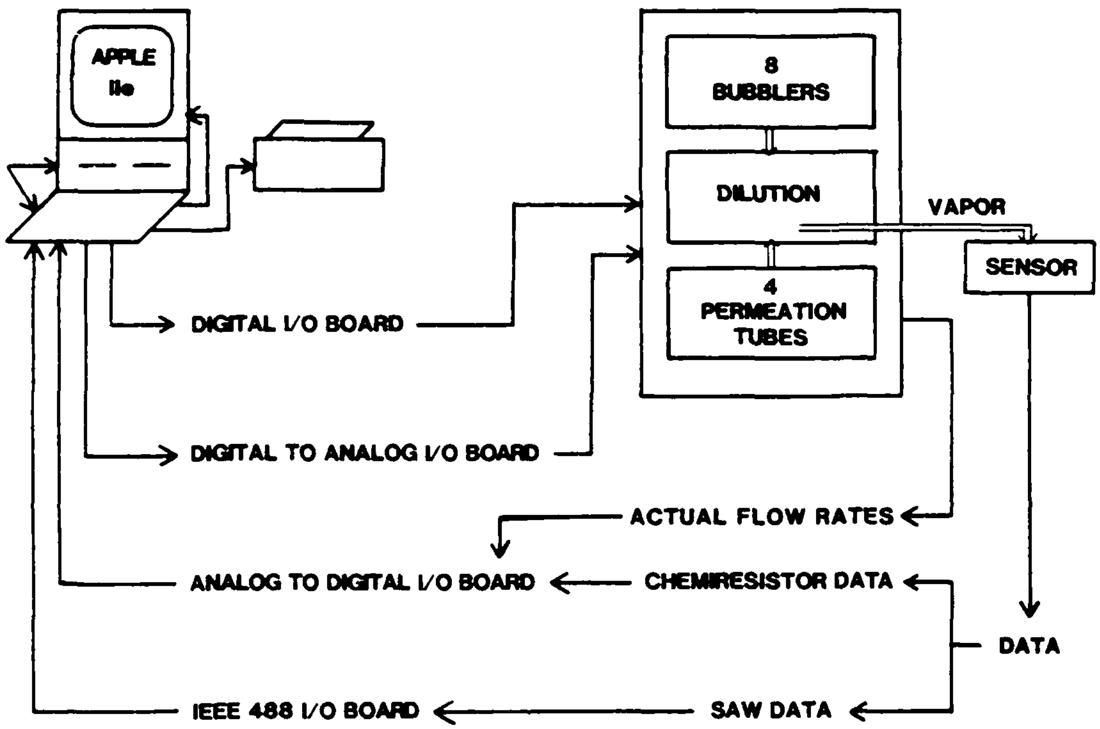


Figure 1. System Interfacing Diagram for the Vapor Generation Instrument

VAPOR FLOW SYSTEM

The vapor flow system is contained in three chassis boxes. Two of these boxes generate vapor streams and the third accepts vapor streams from each of these and from a third optional input. It then dilutes the vapor stream, and reduces the total volumetric flow so that a constant regulated flow rate is output to the sensor. The vapor stream generating boxes will be referred to as the bubbler box and the permeation tube box, and the third box will be called the dilution box. This flow system is diagrammed in Figure 2. The plumbing is constructed using 1/8 inch stainless steel tubing and stainless steel Swagelok fittings throughout, with additional components and exceptions as noted below. Dry air is used as the carrier gas and is supplied to each chassis box at 20-30 psi. Carrier gas flow rates are regulated by mass flow controllers, and the various flow paths are opened and closed by normally closed solenoid valves. Dead volumes between T or cross junctions and valves on those junctions were minimized as much as possible.

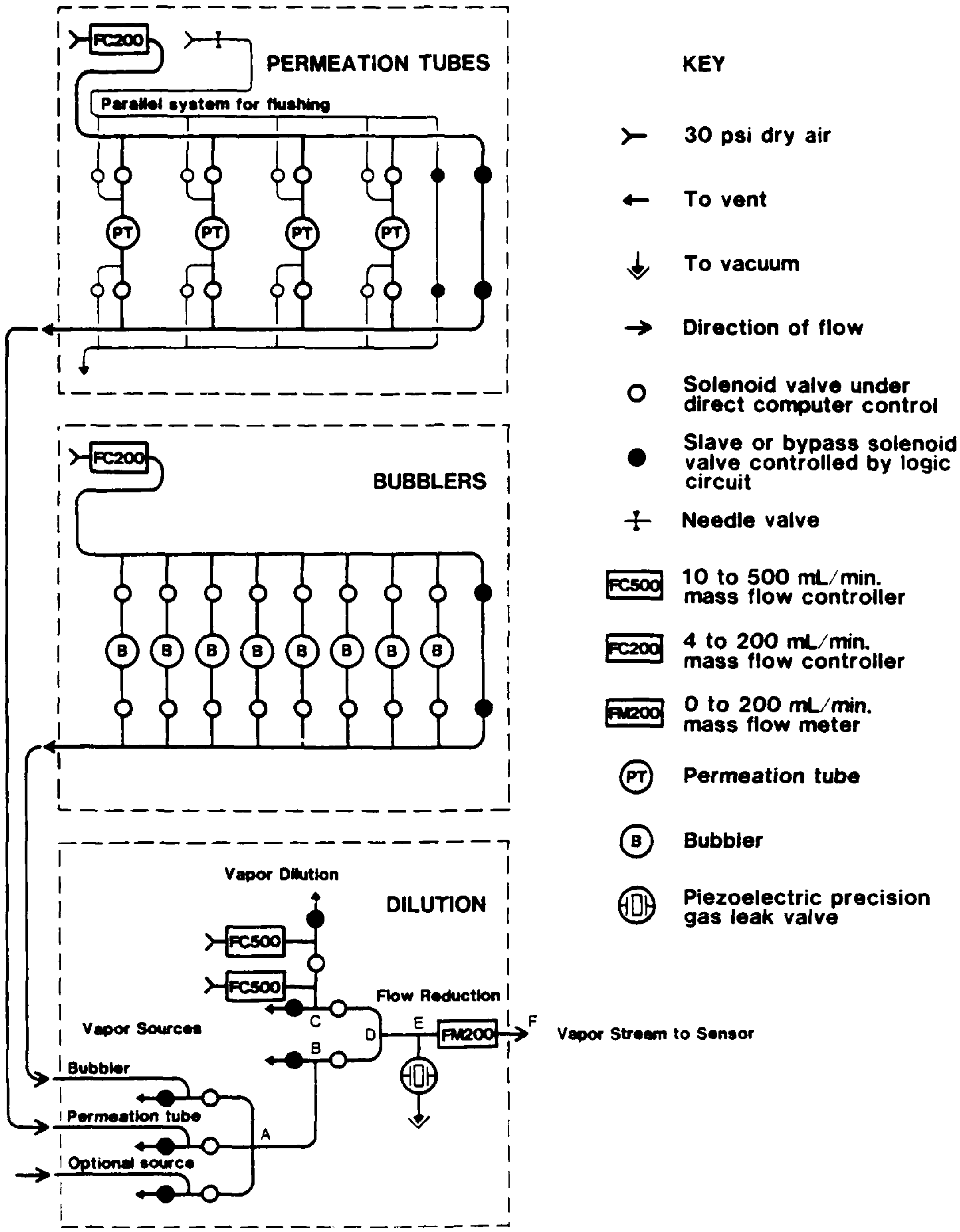


Figure 2. Vapor Stream Flow System

The bubbler box contains eight bubblers which are constructed of 6 3/4 inch lengths of 2 inch O.D. stainless steel pipe, with 1/8 inch thick stainless steel discs (2 inch diameter) welded to the ends. The top end of each has 1/8 inch stainless steel tubing welded into inlet and outlet holes. The inlet tube extends to 1/2 inch from the bottom and the outlet tube is flush with the inside of the top. Air is supplied to the carrier gas loop by a 4-200 mL/min. mass flow controller (FC200), and each bubbler is isolated from the loop by a pair of solenoid valves which are cperated by a single solid state relay. A similar pair of valves, called bypass valves, allow flow through the carrier gas loop when no bubbler is open. When a particular bubbler is chosen as a vapor source, its solenoid valves open, and all other bubbler solenoid valves and the bypass valves are closed.

The permeation tube box contains four permeation tubes, each isolated by a pair of solenoid valves ass the bubblers are. The carrier gas loop is supplied by a 4-200 mL/min. mass flow controller (FC200). A second parallel system of valves and tubing (supplied with air by a needle valve) can flush the permeation tubes to vent when they are not being used. The permeation tubes are either commercial tubes which come equipped with tube fittings, or are teflon permeation tubes made in-house. The latter are contained in a 4 inch hex long nipples (1/2 inch male pipe size) fitted with hex reducing couplings on the ends. These containers could also be used for commercial teflon permeation tubes. All tubes are thermostatted with heating tape and thermocouples and housed in Dewar flasks.

The dilution box contains solenoid valves in master/slave pairs on T junctions, and operate such that the slave will always be contrary to the master. (Please refer to Figure 2.) The flow coming into the T junction will then exit via either the slave valve to a vent, or via the master valve and proceed toward the output to the sensor. One or more of up to three vapor streams can be selected by the dilution box by opening the corresponding master valves preceding point A. The stream or mixture then proceeds to point B. At the same time, dry air from one or two 10-500 mL/min. mass flow controllers (FC500) arrives at point C. If both the master valves at points B and C are open then mixing at point D creates a diluted vapor stream. This stream is split in the flow reduction system at E, and a regulated volume of it proceeds through the mass flow meter (FM 200) at the output, F. If only one of the master valves preceeding point D is open then an undiluted vapor stream or a clean air stream is output by the instrument.

The flow reduction system in the dilution box reduces the total diluted gas flow to a set regulated flow by bleeding the excess flow into vacuum using a piezoelectric precision gas leak valve. This system includes a mass flow meter (FM 200) to measure the actual flow through the path to the output, E to F, and an analog circuit which compares that measured flow to the desired flow (as commanded by the computer). The circuit then adjusts the opening of the gas leak valve until the measured flow matches the desired flow. A schematic diagram of the flow reduction system is shown in Figure 3. With 1/16 inch stainless steel tubing from the T connection to the flow meter and a single

FLOW REDUCTION SYSTEM

THE TOTAL DILUTED VAPOR STREAM IS SPLIT INTO TWO PATHS. A REGULATED VOLUME IS SENT TO THE SENSOR VIA A FLOW METER, AND THE EXCESS IS BLED INTO VACUUM VIA A PIEZOELEECTRIC PRECISION GAS LEAK VALVE.

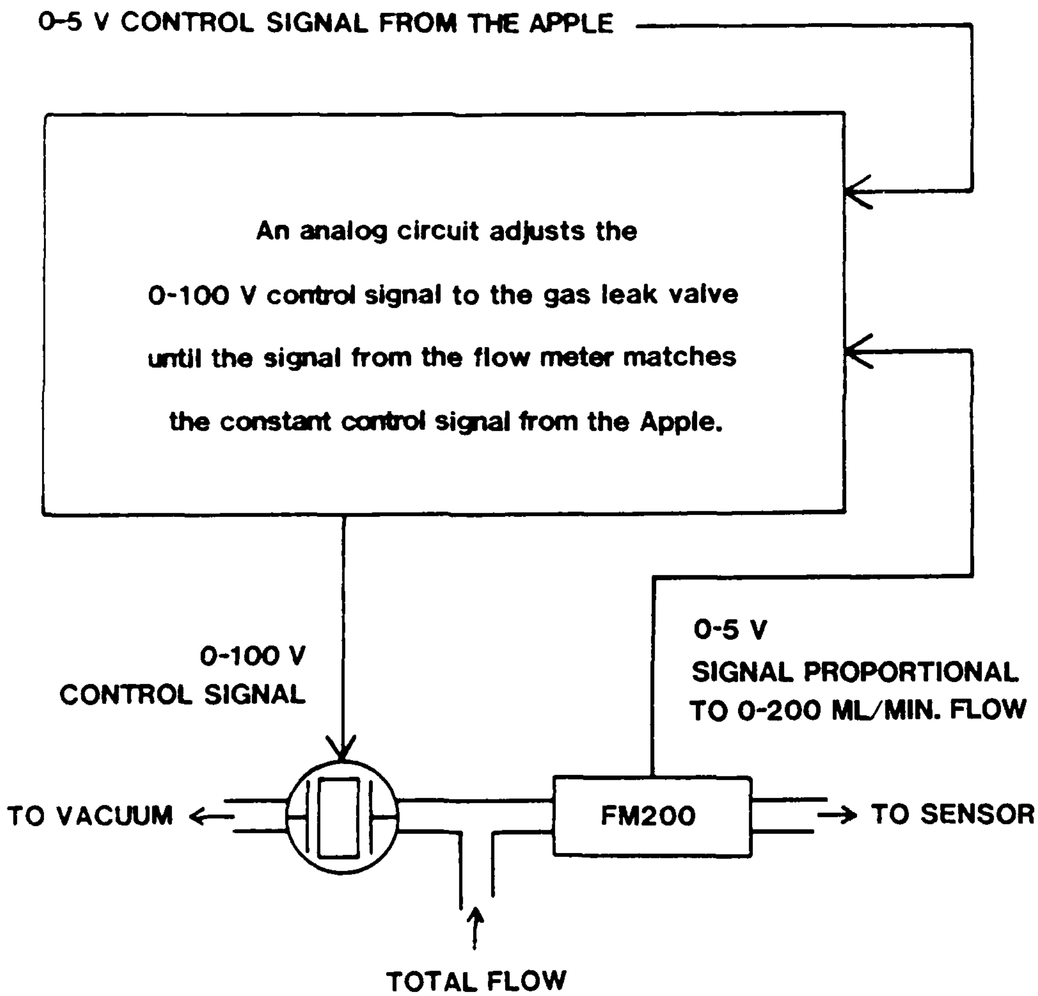


Figure 3. Flow Reduction System

gas leak valve installed the flow reduction system can reduce up to 800 mL/min. arriving at E to 39 mL/min. output at F. With two gas leak valves placed in parallel by having a cross at E instead of a T junction, and 1/8 inch stainless steel tubing from the cross to the flow meter, flow rates in excess of 1200 mL/min arriving at E can be reduced to 39 mL/min. output to F. The system is presently configured in the latter fashion.

ELECTRONIC CONTROL AND INTERFACING

The computer and instrument are powered by surge protected 115 V ac. Specifically, this provides power for the Apple IIe computer and peripherals, solenoid valves, power supplies (+/- 12 V dc, +/- 100 V dc) in the analog circuit of the flow reduction system, power supplies (+- 15 V dc) for the flow controllers and flow meter, and also digital voltmeters which allow various instrument functions to be monitored manually.

I/O boards in the Apple IIe computer operate the instrument and receive flow rate information and sensor response data (see Figure 1). A digital I/O board controls solenoid valves via solid state relays. A digital to analog conversion I/O board sends analog control signals to the flow controllers and to the flow reduction system. An analog to digital conversion I/O board receives flow rate information from the flow meter and flow controllers, and accepts signals from any sensor or sensor system whose output is a voltage (e.g. a chemiresistor [3]). An IEEE-488 I/O board controls and receives data from a frequency counter via the IEEE-488 bus. The frequency counter is used to

measure signals from surface acoustic wave (SAW) sensors [4, 5]. The IEEE-488 bus could also be used with a variety of other instruments, such as electrometers, so that signals from many types of sensors could be monitored with this sensor testing system.

The solenoid valves in the vapor flow system can be divided into two groups, depending on how they are controlled. Those depicted in Figure 2 with open circles are turned on (opened) by solid state relays controlled directly by the computer via the digital I/O board. Those depicted by solid circles are referred to as bypass or slave valves, and are turned on by relays controlled by digital signals generated by logic circuits in each box. A schematic diagram of the signal paths and logic circuits for digital control of the solenoid valves is in Figure 4. The logic circuits are powered by 5 V taken from the digital I/O board. The circuit in the bubbler box functions as an eight input NOR gate whose output controls the bypass valves. If any of the bubblers are open, the bypass opens. Similar four input NOR gates control the bypasses in the permeation tube box. The logic circuit in the dilution box inverts each control signal for a master solenoid valve, and sends the inverted signals to relays controlling the corresponding slave solenoid valves. This circuit causes master/slave valve pairs to operate so that one will always be closed when the other is open. Incorporation of bypass and slave valves controlled by logic circuits assures than an open flow path from each flow controller to either the sensor or a vent is always maintained. This avoids no flow

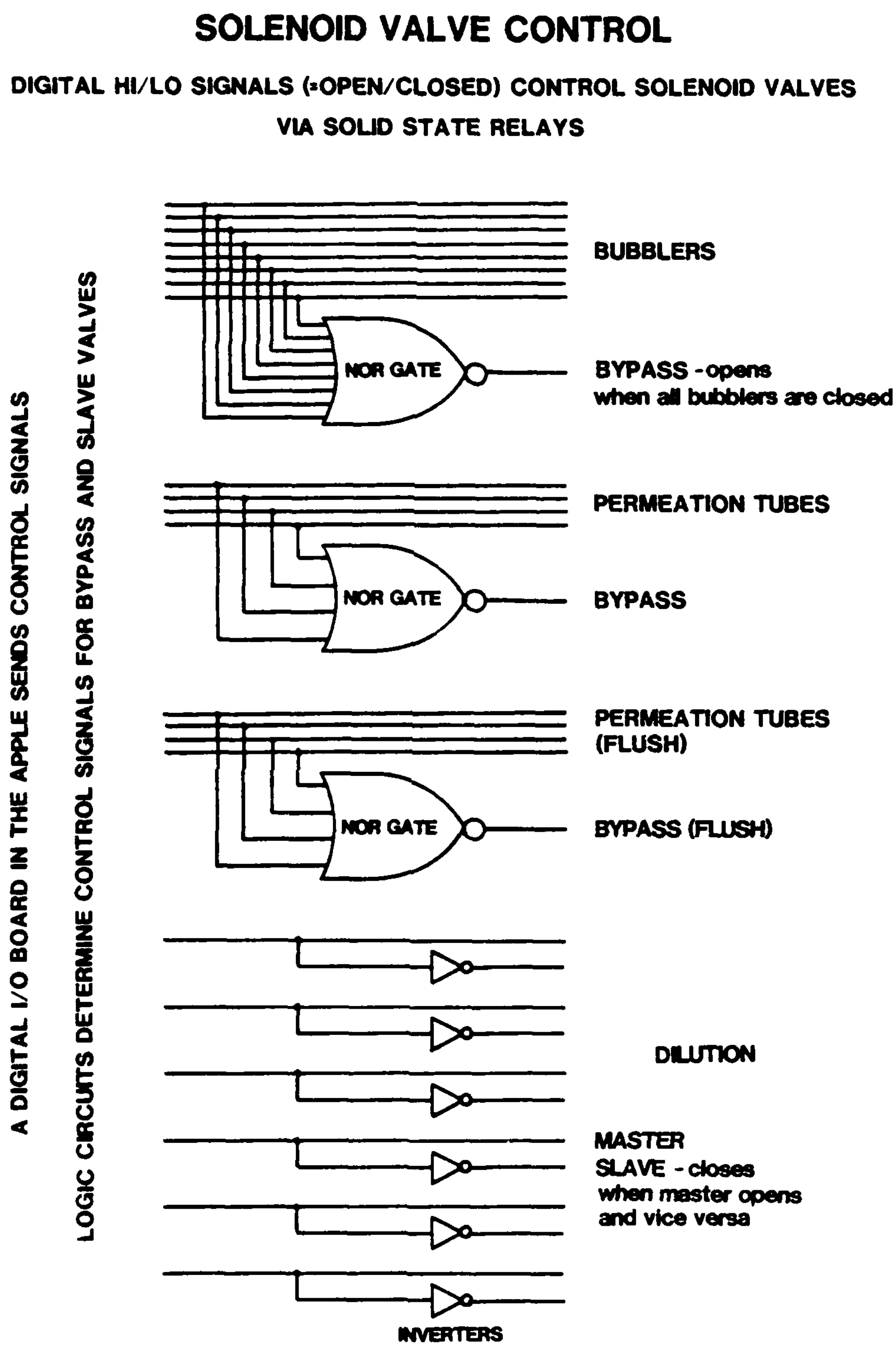


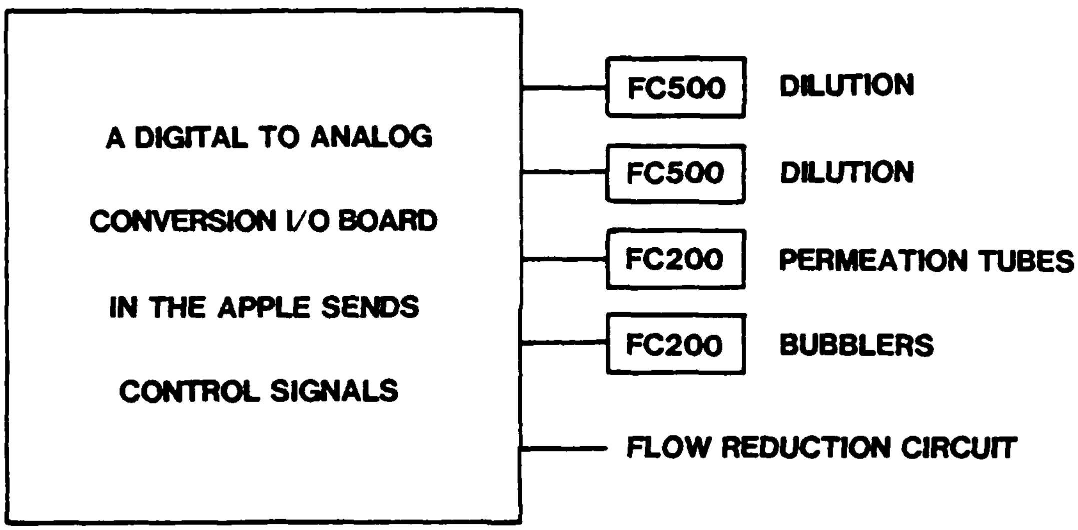
Figure 4. Solenoid Valve Control

conditions in the flow controllers, and continually flushes any part of the system not being used to generate a vapor stream with clean air. Automatic operation of these valves by hardware allows the operator or programmer to concern himself only with those valves leading toward the sensor.

The mass flow controllers are governed by 0-5 V analog signals generated by the digital to analog conversion I/O board. These signals are proportional to the desired flow rate and the range of the flow controller. (for example, a 3.0 V control signal to a FC500 gives 300 mL/min. flow.) In addition, the flow controllers and the flow meter contain flow sensors which output 0-5 V analog signals proportional to the measured rate of flow through them. The use of analog control signals for controlling flow rates is shown in Figure 5. The flow reduction system incorporates an analog circuit which compares the difference between the flow meter output and 0-5 V analog control signal (proportional to the desired flow and the flow meter range) generated by the digital to analog conversion I/O board (see Figure 3). This difference is determined, integrated, and amplified to a 0-100 V range by a series of three operational amplifiers. The output of the third op amp is prevented from going negative by a diode, and it is this 0-100 V signal that controls the gas leak valve. The input from the flow meter is clamped to 6 V by a zener diode, allowing the automatic operation of this circuit to be over-ridden and the gas leak valve to be shut, regardless of high flow rates through the flow meter, by sending a control signal in excess of 6V (typically 10 V).The

FLOW CONTROLLER AND FLOW REDUCTION SYSTEM CONTROL

0-5 V ANALOG SIGNALS SET THE DESIRED FLOW RATES



Flow controllers regulate flow according to 0-5 V signals proportional to flow controller range, e.g. for FC500, 2.5 V = 250 ml/min.

The signal to the flow reduction circuit dictates the desired flow to the sensor, 0-5 v proportional to the 0-200 ml/min. range of the flow meter(FM200).

Flow controllers also output a separate 0-5 V signal which indicates the actual flow. This signal should match the control signal.

Figure 5. Flow Controller and Flow Reduction System Control

instrument has also been equipped with three digital volt meters. These are wired in so that the flow rates through the flow meter and flow controllers can be monitored manually. Test points in the flow reduction system at the outputs of the differential and integrating op amps can also be monitored.

VAPOR STREAM OPERATIONS AND CALIBRATION

This instrument permits setting up a vapor stream and switching the output between clean air and vapor stream as follows. (Please refer to Figure 2). First the desired flow rates to all the flow controllers are commanded by the computer, and the solenoid valve pair for the selected vapor source, e.g. a bubbler, is opened. The resulting vapor stream proceeds into the dilution box and is selected by opening one of the master valves preceding point A. It then proceeds through the open slave valve at point B to vent. At the same time, the flow from one or two of the FC500 flow controllers proceeds from point C via D to point E, the flow reduction system. The flow rates for these flow controllers have been set according to the degree of dilution desired. A regulated volume of the clean air stream is output to F by the flow reduction system. This initial set up of flow rates is one of the times that the flow reduction system must adjust the opening of the gas leak valve to vacuum so that the output to the sensor will be at the flow rate commanded by the computer. At this point the vapor stream is equilibrating and going to vent and clean air is being output by the instrument. The command signals to the mass flow controllers and

the flow reduction system will not be changed until another vapor or concentration is to be set up.

Swi ching from clean air to a vapor stream is accomplished entirely by opening and closing solenoid valves. The particular solenoid valves changed for this purpose depends on the degree of dilution which has been set up. If the vapor stream coming into the dilution box is to proceed undiluted to the output, then the initial flow of dilution air going to D comes entirely from the FC500 closest to point C, and its flow rate has been set to be the same as the flow rate of the vapor stream arriving at B (and going to vent). The clean air output by the instrument is switched to undiluted vapor stream by opening the master valve at B and closing the master valve at C. This switching operation does not change the flow rate of the gas stream arriving at the flow reduction system and the gas leak valve does not need to make any adjustment to maintain the commanded output flow rate.

If the vapor stream is to be diluted with less than 500 mL/min of air, then the FC500 farthest from C is set to match the flow rate of the vapor stream. The FC500 closest to C provides all the air desired for dilution. When clean air is being output the vapor stream exits to vent at B and clean air from both FC500s proceeds from C to the flow reduction system. When the vapor is switched on by opening the master valve at B, the flow from the FC500 farthest from point C is switched off (to vent), and the flow rate arriving at the flow reduction system does not change.

When the vapor is diluted with greater than 500 mL/min. of air, then the combined flow rate from both the FC500 flow

controllers is set to the flow of air needed for the dilution. This flow always proceeds from C via D to E. Clean air is switched to dilute vapor stream by simply opening the master valve at B. The flow reduction must readjust the gas leak valve in this case because this switching mechanism increases the flow rate arriving at E. This adjustment is minor, however, because the added vapor stream flow is smaller than flow of dilution air for which the system has already adjusted.

In practice, the flow reduction system will sometimes also make adjustments when the clean air is switched to vapor even though the volume of air arriving at E has not been changed, i.e. when the vapor stream is undiluted or is diluted by less than 500 mL/min. of air. This occurs because the mass flow meter in the flow reduction system is calibrated for dry air, and gives an erroneous reading when high concentrations of a vapor with thermal properties differing from those of air are sent through it. The flow reduction system automatically adjusts the gas leak valve so that the reading from the flow meter will return to the desired value, even though that reading is misstating the actual flow. This error becomes negligible when the vapor stream is very dilute.

The range of dilution possible with this instrument depends on the minimum flow rate to be output to the sensor and the maximum total flow rate allowed by the flow controllers. Total flow rate is defined as the flow rate arriving at point E, or as the total volumetric flow in which the total mass flow of vapor is contained. These are different from the actual flow which is output to the sensor when the flow reduction system is operating.

A flow rate of 39 mL/min. was chosen to be output to the sensor, and this value also becomes the minimum flow sent past a permeation tube or through a bubbler. The maximum dilution possible for a permeation tube occurs when its mass flow is diluted into 200 sccm from the permeation tube box FC200 plus 500 sccm from each FC500 in the dilution box. The most dilute vapor stream is therefore 3% (= 39/1200) of the most concentrated vapor stream from a permeation tube.

Unlike the permeation tubes, the mass flow from a bubbler varies with the volumetric flow through it. The latter flow is always held constant at 39 sccm and all dilution is accomplished by adding volumetric flow from the two FC500's. This determines a maximum dilution to 4% (= 39/1039) of the concentration of the most concentrated vapor stream from a bubbler.

The uncertainty in the total flow rate is determined by the uncertainties of flow rates of those flow controllers which are contributing to the total flow. The flow controllers installed in this instrument are accurate to 1% of full scale flow, e.g. mL/min. for an FC500 (and repeatable to 0.2% of full scale). The percent uncertainty in total flow is, therefore, the least when the number of flow controllers contributing to the total flow is minimized and when low flow conditions are avoided through any of those flow controllers (especially FC500's). In many cases, a particular dilution could be achieved by more than one method with this instrument, so the above factors were considered in order to select the best method. For example,

diluting the mass flow from a permeation tube with increasing amount of volumetric flow form the permeation tube FC200 (up to 200 mL/min. is more precise than diluting 39 mL/min. of flow from the permeation tube box with additional volumetric flow from an FC500 in the dilution box.

In practice, a menu of possible dilutions for each type of vapor source (permeation tube or bubbler) is provided for the operator. The choices available and the specifics on how they are accomplished by instrument hardware have been set up to maximize the precision in the total flow rate. Table 1 provides examples of dilution information associated with selected menu choices for permeation tubes. Sixteen choices are available from undiluted vapor stream to maximum dilution, each choice being approximately 80% of the concentration of the choice before it. The maximum uncertainty occurs in the case of undiluted vapor stream, and is 5%. The uncertainty is only 1% at maximum dilution. The menu for bubblers was set up similarly but certain choices were eliminated due to high uncertainties. The uncertainty is 5% for undiluted vapor stream, and then increases sharply when volumetric flow from an FC500 is added to the 39 mL/min. of the bubbler vapor stream. The next choice provided on the menu is 40% of the undiluted concentration, with an uncertainty of 7%, the largest uncertainty of any choice in either menu. The uncertainty is below 5% for bubbler dilution choices below 25% of maximum concentration, and is near 1% at the maximum dilution. The mass flow rates from all vapor sources were calibrated gravimetrically. Commercial permeation tubes

TABLE 1. Selected Permeation Tube Dilution Menu Choices

Menu Choice #	Flow Controller Flow Rates mL/min.			Total Volumetric Flow Rate[a] mL/min.	Fractional Concentration[b]
	FC200[c]	FC500	FC500		
1	39±2	0[d]	0	39±5.1%	1.000
2	48±2	0	0	48±4.1%	.805
4	77±2	0	0	77±2.6%	.509
8	195±2	0	0	195±1.0%	.200
12	200±2	254±5	0	454±1.5%	.086
16	200±2	500±5	500±5	1200±1.0%	.033

a The sum of the volumetric flow rates from all contributing flow controllers.

b Fractional concentration relative to the concentration when the mass flow is carried by 39 mL/min. of carrier gas.

c FC200 in the permeation tube box. Flow from the FC200 in the bubbler box is not used to dilute permeation tube vapors.

d Zeros indicate that this flow controller does not contribute flow or uncertainty to the total flow.

were purchased already calibrated. Teflon permeation tubes produced in-house were calibrated by determining mass loss as a function of time at the temperature at which they were to be used. Bubblers were calibrated by adsorbing the vapor mass flow on activated carbon and determining the mass increase of the carbon. This procedure was carried out with the bubblers installed in the instrument at ambient temperatures with a carrier gas flow rate of 39 mL/min. Mass flow rates were stable after fifteen minutes of bubbling. Successive determinations resulted in mass flow rates with errors of less than 6% for bubblers and less than 10% for permeation tubes made in house. The mass flow rates from bubblers varied by as much as 30% from rates calculated from published vapor pressures and the ideal gas law. The observed mass flow rates were sometimes greater than the estimated values indicating that the difference between observed and estimated values is not due to a failure to saturate the carrier gas.

The uncertainty in the volume of the diluted vapor stream actually sent to the output to the sensor (F) is dependent on a variety of electronic factors, including the uncertainty in the measurement of flow from the FM200, and uncorrected offsets in the analog circuit which controls the system. However, these uncertainties have no affect on the precision of the concentration of vapor in the flow output to the sensor. In practice, actual flow rate output is generally within 5% of the set value, 39 mL/min.

SOFTWARE AND OPERATION

Two computer programs in BASIC set up and run sequences of vapor stream generation/sensor exposure experiments. These programs are outlined in Table 2. The first program is a user

Table 2. Software for Sensor Testing

Program 1

1. Update vapor source mass flow rates.
2. Calculate menus of concentration choices for each vapor.
3. User selects vapor/concentrations to be generated.
4. Text file stored on disk for each selection.

Program 2

1. Flush flow system, output clean air.
2. Read first text file.
3. Generate and equilibrate vapor stream, output clean air.
4. Test sensor, output clean air, then vapor, then air.
5. Store data on disk.
6. More experiments?
   No - Flush flow system, output clean air, end.
   Yes- Read next text file.
7. Is the next vapor different?
   No - Adjust dilution air, loop to step 4.
   Yes- Flush flow system, loop to step 3.

interactive program that contains information on all the vapor sources in use and menus offering the dilution choices described above. The user chooses the vapors and concentrations to be generated by the instrument, and supplies information on the sensor being tested. For each experiment (i.e. vapor and concentration), a text file is stored on disk which contains the

following information: the sensor being tested, the vapor and concentration to be generated, values for variables that dictate which solenoid valves must be opened, and values for variables that determine the flow rates which the flow controllers will set up in order to generate the chosen vapor stream at the chosen concentration.

The second BASIC program operates the instrument and performs the experiments contained in the text files on disk. The instrument is started with clean air flowing throughout the plumbing system and the first text file is read. The desired vapor stream and dilution is set up as described previously, the vapor stream is allowed to equilibrate for twenty minutes (while it exits to vent), and the baseline response of the sensor under clean air is monitored. Sensor response and recovery are than tested by alternately switching the instrument output between vapor and clean air. At the same time, the sensor response is displayed graphically on the computer monitor. At the completion of the experiment, the test conditions and data are stored on disk, the graphics are dumped to the printer, and the next text file is read from disk. If the next vapor is different form that of the previous experiment, the system is flushed with clean air for ten minutes before generating and equilibrating the new vapor stream. If the next vapor is the same but at a different concentration, then the flow rates are adjusted for the new concentration and the experiment proceeds. The cycle of reading the experiment from disk, performing the experiment, and saving the data on disk is repeated until all the experiments have been

completed. The system is then flushed with clean air until the operator shuts it down.

CONCLUSION

The instrument described above has proven to be extremely valuable in conducting chemical sensor research. Previously untested sensor coating materials are now rapidly screened against a range of chemical vapors. The capability to generate multiple concentrations of a single vapor, and to maintain a constant flow rate to the sensor regardless of the dilution required to achieve the desired concentration, allows calibration curves to be determined very conveniently. Extended sequences of tests involving target vapors at low concentrations, potential interferents at high concentrations, and mixtures of two vapors are automaticallY executed to critically evaluate promising prototype sensors. Testing sequences requiring days of continuous operation are routinely conducted. The generation of sensor data sets of sufficient size for the application of pattern recognition techniques is readily manageable task. A matrix of surface acoustic wave sensor data which was collected with this instrument and analyzed by pattern recognition techniques has recently been reported [5].

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REFERENCES

1. R.S. Barratt, "The Preparation of Standard Gas Mixtures: A Review," *The Analyst*, **106** (1981) 817-849.

2. J. Namiesnik, "Permeation Devices for the Preparation of Standard Gaseous Mixtures," *Chromatographia*, **17** (1983) 47-48, and references therein.

3. H. Wohltjen, W.R. Barger, A.W. Snow, and N.L. Jarvis, "A Vapor-Sensitive Chemiresistor Fabricated with Planar Microelectrodes and a Langmuir-Blodgett Organic Semiconductor Film," *IEEE Transactions on Electron Devices*, **ED-32** (1985) 1170-1174.

4. H. Wohltjen, "Mechanism of Operation and Design Considerations for Surface Acoustic Wave Device Vapor Sensors," *Sensors and Actuators*, **5** (1984) 307-325.

5. D.S. Ballantine, Jr., S.L. Rose, J.W. Grate, and H. Wohltjen, "Correlation of Surface Acoustic Wave Device Coating Responses with Solubility Properties and Chemical Structure Using Pattern Recognition," *Anal. Chem*, **58** (1986) 3058-3066.

APPENDIX

The following is a compilation of some of the components used in the vapor-generation instrument and suppliers for those components. In many cases, satisfactory alternative components or suppliers may exist. This compilation is meant only to indicate the components used and where replacement parts could be obtained.

Mass flow controllers and mass flow meters are series FC260 and FM360 respectively, purchased from Tylan, 23301 S. Wilmington Ave., Carson, CA 90745, (213) 518-3610.

Solenoid valves are #A2013-120VAC, A20 series 2 way normally closed solenoid valve, stainless steel, grommet housing, 1/16" orifice purchased from Precision Dynamics, 60 Production Court, New Britain, Connecticut, 06051, (203) 229-3753. The standard O-rings and plunger seals swell in organophosphorous solvents and vapors, which can cause valves to fail to open. Replacement plungers with Kalrez (PF) seals and replacement O-rings of ethylene propylene rubber (EPR) do not suffer swelling in dimethyl methylphosphonate and were installed. Valves already containing these improved material can be ordered as #A2013-PF-120VAC, specify EPR O rings. Kalrez is a fluoro elastomer. The standard O-rings are "nitrile".

The piezoelectric precision gas leak valve was purchased from Vacuum Accessories Corporation, 390 Central Ave., Bohemia, N.Y. 11716, (516) 589-6464.

The solid state relays used are Teledyne Relays, Hawthorne CA 90250, PIN: 611-7 which are optically isolated, 10 amp, 140VAC output, 3-28 VDC control. These can be purchased from electronic suppliers, for example Pioneer/Washington, 9100 Gaither Rd., Gaithersburg, MD 20760, (301) 921--0660.

The IEEE-488 interface card is an Apple product, available through dealers that sell Apple computers. Digital I/O boards, digital to analog I/boards and analog to digital I/O boards for Apple Computers are available through Applied Engineering, P.O. Box 798< Carrollton, TX 75006, (214) 241-6060.

Permeation tubes were purchased from GC Industries, Inc., 20361 Prairie St. #4, Chatsworth, CA 91311, (818) 701-7072. Other suppliers for permeation tubes include Analytical Instrument Development, Inc., Rt. 41 and Newark Rd., Avondale, PA 19311, (215) 268-3181a, and VICI Metronics, 2991 Corvin Drive, Santa Clara, CA 95051, (408) 737-0550.

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